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An Efficient Cleavage and Fries Rearrangement of Esters with Aluminium Triiodide

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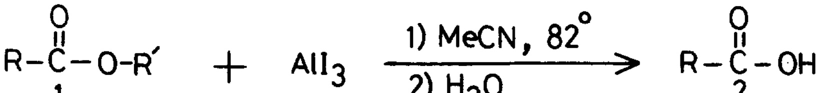
Abstract: Aluminium triiodide efficiently cleaved esters to carboxylic acids and converted phenyl benzoate to o- and p-hydroxybenzophenones via Fries rearrangement.

Esters constitute an important protecting group in organic synthesis. Despite numerous methods available, however the deprotection of esters to carboxylic acids attracts considerable attention because a general method[1] for different kinds of esters is still obscure. In addition, a large number of carboxylic esters are sensitive to strongly acidic or basic hydrolysis, which consequently stimulated interest for the search of more efficient and milder ester cleaving reagents[1,2]. Recently we have discovered the utility of aluminium triiodide as a potential reagent for deoxygenation of organic N-oxides[3] and dehydration of oximes[4]. Here we wish to report the use of aluminium triiodide as an ideal reagent for cleavage of a variety of carboxylic esters to acids.

In a typical procedure, ester (1a)(0.001 mol) was added to a freshly prepared aluminium triiodide (0.002 mol) in dry acetonitrile (50ml), the mixture was refluxed for 0.5 h, concentrated and poured into ice cold water. Extraction with ethylacetate and removal of solvent gave the carboxylic acid (2a) in 88% yield.



$$\underset{\underline{1}}{R-\overset{O}{\overset{\|}{C}}-O-R'} + AlI_3 \xrightarrow[2)\ H_2O]{1)\ MeCN,\ 82^\circ} \underset{\underline{2}}{R-\overset{O}{\overset{\|}{C}}-OH}$$

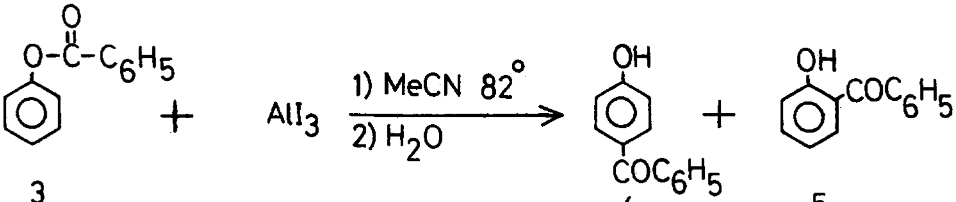
	a	b	c	d	e
R	C_6H_5	2,4-Cl_2-C_6H_3	$CH_3(CH_2)_2$	C_6H_5-CH=CH	C_6H_5-C≡C
R'	CH_3	C_2H_5	CH_3	CH_3	C_2H_5

The aliphatic, olefinic and acetylenic esters (1c-e), similarly on treatment with aluminium triiodide afforded corresponding carboxylic acids (2c-e) in high yields (table)[5]. The deprotection of all esters have been found to be rapid and selective.

Table : Cleavage of Esters with Aluminium Triiodide

Compound	R	Yield (%)	Time (h)	mp or bp (°C)
2a	C_6H_5	88	0.5	122 - 123
2b	$2,4\text{-}Cl_2\text{-}C_6H_3$	90	0.5	157 - 160
2c	$CH_3(CH_2)_2$	75	0.5	161 - 162
2d	$C_6H_5\text{-}CH=CH$	85	0.5	132 - 133
2e	$C_6H_5\text{-}C\equiv C$	80	0.5	135 - 137

However, phenylbenzoate (3) reacted with aluminium triiodide in acetonitrile under reflux for 10h, to afford o- and p-hydroxybenzophenones (4 and 5)(o/p : 1/2 ratio) via Fries rearrangement[6] in 70% yield.



3 4 5

In summary, we have developed a new general methodology for the selective and mild cleavage of different kinds of carboxylic esters and Fries rearrangement of phenol esters.

References and Notes

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